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[Title of the Invention] CELL ELECTRODE AND ELECTROCHEMICAL CELL THEREWITH

[Features of the Invention]

[Claims]

[Claim 1] A cell electrode for an electrochemical cell in which an active material in an electrode material is a proton-conducting polymer, wherein the electrode material comprises a nitrogen-containing heterocyclic compound.

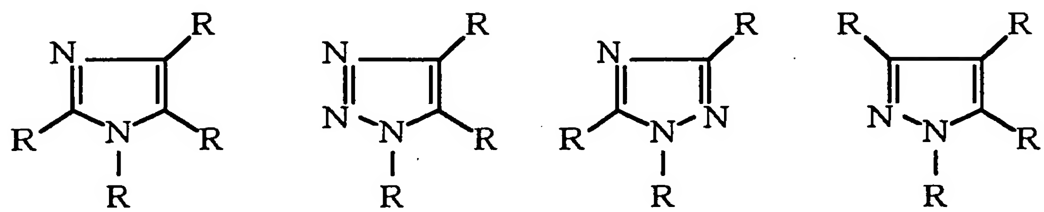
[Claim 2] A cell electrode for an electrochemical cell in which an active material in an electrode material is a proton-conducting polymer, wherein the active material in the electrode material is a proton-conducting nitrogen-containing basic polymer obtained by the copolymerization of a nitrogen-containing heterocyclic compound and the material for the above proton-conducting polymer.

[Claim 3] The cell electrode as claimed in Claim 1 or 2, wherein the nitrogen-containing heterocyclic compound is one or more selected from the group consisting of the nitrogen-containing heterocyclic compound monomers and the nitrogen-containing basic polymers.

[Claim 4] The cell electrode as claimed in Claim 1 or 2, comprises the copolymer material as claimed in Claim 2.

[Claim 5] The cell electrode as claimed in Claim 3, wherein the nitrogen-containing heterocyclic compound monomer is at least one selected from the group consisting of imidazole and its derivative represented by formula (1),

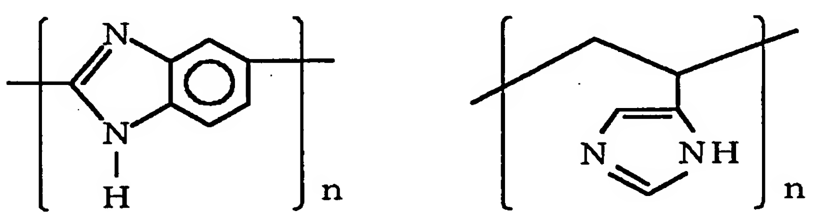
triazole and its derivative represented by formula (2) or (3) and pyrazole and its derivative represented by formula (4):



(1) (2) (3) (4)

wherein Rs independently represent hydrogen, alkyl having 1 to 4 carbon atoms, amino, carbonyl, nitro, phenyl, vinyl, halogen, acyl, cyano, trifluoromethyl, alkylsulfonyl or trifluoromethylthio.

[Claim 6] The cell electrode as claimed in Claim 3, wherein the nitrogen-containing basic polymer is at least one selected from the group consisting of polybenzimidazole, polyvinylimidazole, polybenzbisimidazole and polyimidazole, besides polybenzimidazole represented by formula (5) and polyvinylimidazole represented by formula (6):



(5) (6)

wherein n represents a positive integer.

[Claim 7] The cell electrode as claimed in any one of

Claims 1 to 6, wherein the content of the nitrogen-containing heterocyclic compound and the nitrogen-containing basic polymer amounts to 1 to 80 wt% to 100 wt% of the active material.

[Claim 8] A secondary battery wherein at least one of the electrodes is the electrode as claimed in any one of Claims 1 to 6, which comprises a proton-conducting polymer as an active material.

[Claim 9] A capacitor wherein at least one of the electrodes is the electrode as claimed in any one of Claims 1 to 6, which comprises a proton-conducting polymer as an active material.

[Detailed Description of the Invention]

[0001]

[Technical Field to which the Invention Pertains]

This invention relates to an electrode used in an electrochemical cell such as a secondary battery and an electric double-layer capacitor and an electrochemical cell using the electrode. In particular, it relates to an electrode having improved cycle properties without reduction in an appearance capacity, and an electrochemical cell using the electrode.

[0002]

[Prior Art]

There have been suggested and practically used electrochemical cells (hereinafter, referred to as "cell") such as secondary batteries and electric double-layer

capacitors in which a proton-conducting polymer is used as an electrode active material. Such a cell is illustrated in a cross-sectional view of FIG. 1.

[0003]

Specifically, FIG. 1 shows a cell where a positive electrode 2 containing a proton-conducting polymer as an active material is formed on a positive current collector 1 while a negative electrode 3 is formed on a negative current collector 4, and these electrodes are combined via a separator 5 and where only protons are involved in an electrode reaction as a charge carrier. Also, the cell is filled with an aqueous or non-aqueous solution containing a proton source as an electrolytic solution, and is sealed by a gasket 6.

[0004]

The electrodes 2, 3 are formed as follows. A powdery doped or undoped proton-conducting polymer is blended with a conductive auxiliary and a binder to prepare a slurry, which is then placed in a mold and molded by a hot press to form an electrode having a desired electrode density and a desired film thickness. Then, a positive electrode and a negative electrode thus formed are mutually faced via a separator to give a cell.

[0005]

Examples of a proton-conducting polymer used as an electrode active material include π-conjugated polymers such as polyaniline, polythiophene, polypyrrole,

polyacetylene, poly-p-phenylene, polyphenylene-vinylene, polyperinaphthalene, polyfuran, polyflurane, polythienylene, polypyridinediyl, polyisothianaphthene, polyquinoxaline, polypyridine, polypyrimidine, polyindole, indole trimer, polyaminoanthraquinone and their derivatives; and hydroxyl-containing polymers such as polyanthraquinone and polybenzoquinone where a quinone oxygen is converted into a hydroxyl group by conjugation. These compounds may be doped to form a redox pair exhibiting conductivity. These polymers are appropriately selected as a positive active material and a negative active material, taking a redox potential difference into account.

[0006]

Known electrolytic solutions include an aqueous electrolytic solution consisting of an aqueous acid solution and a non-aqueous electrolytic solution based on an organic solvent. When using a proton-conducting polymer, the former aqueous electrolytic solution is preferentially used because it can give a high-capacity cell. The acid used may be an organic or inorganic acid; for example, inorganic acids such as sulfuric acid, nitric acid, hydrochloric acid, phosphoric acid, tetrafluoroboric acid, hexafluorophosphoric acid and hexafluorosilicic acid and organic acids such as saturated monocarboxylic acids, aliphatic carboxylic acids, oxycarboxylic acids, p-toluenesulfonic acid, polyvinylsulfonic acid and lauric acid.

[0007]

A cell using such a proton-conducting polymer as an electrode active material has a short cycle life due to increase in an internal resistance, and the tendency becomes more prominent as a temperature is elevated. Furthermore, it has a drawback of insufficient long term stability under a high temperature atmosphere.

[0008]

These problems are caused by aggravated deterioration atmosphere due to deceleration of proton adsorption-desorption reaction as a charge/discharge mechanism of an electrode active material. In particular, at an elevated temperature, peroxidation of a material is much more accelerated, resulting in accelerated deterioration.

[0009]

An electrode active material is susceptible to deterioration in an oxidized state. It is probably because a proton ($H^+$) adsorption-desorption reaction for the active material is deteriorated over time in the charge/discharge mechanism as described below. Such deterioration proceeds because doping/dedoping activity of the active material is reduced under an excess proton atmosphere rather than an optimal proton atmosphere which depends on the identity of the active material and the number of reaction electrons, in a proton adsorption-desorption reaction between the active material and an electrolyte. Thus, charge/discharge

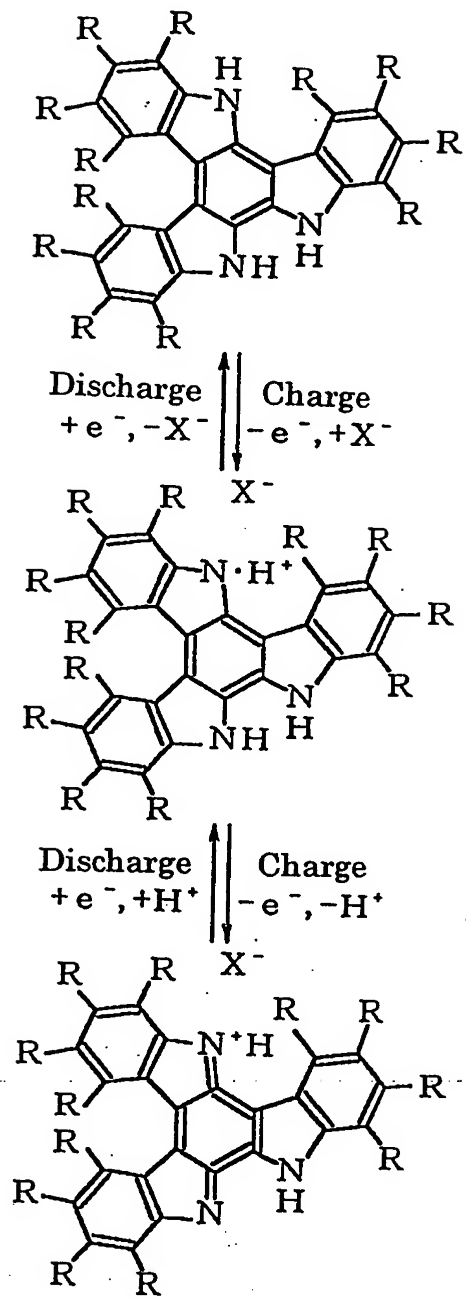
power of the cell is deteriorated. It is called "peroxidation-perreduction deterioration"; specifically, peroxidation deterioration for an active material of positive electrode and perreduction deterioration for an active material of negative electrode.

[0010]

This phenomenon will be described for a case where an active material of positive electrode is an indole polymer (indole trimer) while an active material of negative electrode is a quinoxaline polymer. Herein, charge/discharge mechanisms for a positive and a negative electrode materials are as indicated in chemical formulas (7) and (8), respectively, wherein Rs represent appropriate substituents and X represents an anion.

[0011]

Positive electrode

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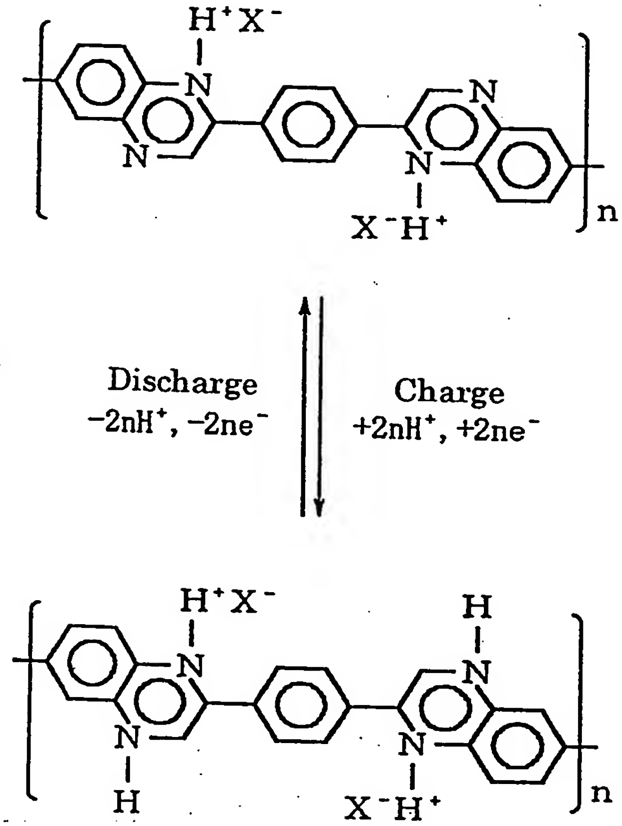
Negative electrode

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[0012]

Under a high-level acid atmosphere (low pH), the phenomenon particularly tends to occur so that deterioration in cycle properties is accelerated. For polyphenylquinoxaline which can be used as a material of negative electrode, tetraprotonation may be caused whereas a normal doped state is represented by a diprotonated derivative in a charge/discharge mechanism. Thus, the active material is dissolved, leading to reduction in a charge/discharge power. An excessively higher electrolyte concentration (proton concentration) may further accelerate oxidation deterioration.

[0013]

FIG. 6 is a graph showing variation in cycle properties to an electrolyte concentration (sulfuric acid concentration). As seen in this graph, as an electrolytic solution concentration increases, a capacity rate decreases according to the cycle number so that cycle properties are deteriorated. In addition, under a low concentration atmosphere, cycle properties are improved while an appearance capacity tends to be reduced. FIG. 7 is a graph illustrating variation in an appearance capacity to an electrolyte concentration (sulfuric acid concentration). As seen in this graph, as an electrolyte concentration is reduced, an appearance capacity is reduced.

[0014]

Electrolytic solutions comprising a nitrogen-

containing heterocyclic compound as a non-aqueous electrolytic solution in the prior art have been described in Japanese Laid-open Patent Publication Nos. 2000-156329 (Prior art 1) and 2001-143748 (Prior art 2). Japanese Laid-open Patent Publication No. 7—320780 (Prior art 3) has described a solid-electrolyte secondary battery comprising a polymer gel electrolyte consisting of, for example, an aprotic solvent and polyimidazole. Japanese Laid-open Patent Publication No. 10-321232 (Prior art 4) has described an electrode comprising a benzimidazole derivative although an electrolytic solution used therein is different from that in this invention.

[0015]

In Prior art 1, there has been disclosed an electrolytic solution for an aluminum electrolysis capacitor comprising a quaternary cation from a compound containing N,N,N'-substituted amidine group and an organic solvent of an organic acid anion. There has been described that although a conventional electrolytic solution comprising a quaternary ammonium carboxylate has a drawback that degradation of a rubber packing is accelerated so that sealing performance is significantly deteriorated, an additive having a cationic, quaternary amidine group may improve thermal stability of the electrolytic solution and a specific conductivity, and that in particular, a compound in which electrons in the amidine group are delocalized and a cation is stabilized by resonance gives an improved

specific conductivity because of accelerated ion dissociation. There has been further described that when excess hydroxide ions are generated after electrolysis in the electrolytic solution, the hydroxide ions may rapidly disappear by reaction of the hydroxide ions and the amidine group so that unlike a conventional quaternary ammonium salt, effects of the electrolysis can be reduced and thus degradation of a packing in a capacitor can be minimized, resulting in improved sealing performance.

[0016]

Prior art 2 has disclosed an electrolytic solution for a non-aqueous electrolyte lithium secondary battery, comprising a lithium salt of a perfluoroalkylsulfonic acid dissolved in an organic solvent and at least one selected from heterocyclic compounds containing at least one fluorine atom and a nitrogen or oxygen atom. According to Prior art 2, the heterocyclic compound added to the electrolytic solution can form a strongly adsorptive and antioxidative film on a positive current collector, resulting in preventing oxidation deterioration of the positive current collector and thus improvement in cycle properties.

[0017]

Prior art 3 has disclosed a solid electrolyte secondary battery comprising a positive electrode, a negative electrode containing lithium as an active material, and a polymer solid electrolyte consisting of a complex of

an electrolyte salt with a polymer or a polymer gel electrolyte prepared by impregnating an electrolytic solution of an electrolyte salt dissolved in an aprotic solvent into a polymer, wherein the polymer is selected from the group consisting of a polyamide, polyimidazole, a polyimide, polyoxazole, polytetrafluoroethylene, polymelamineformamide, a polycarbonate and polypropylene. There is described that cycle properties are improved because the electrolyte is unreactive to the negative electrode and thus an internal resistance is unlikely to be increased even after repeating charge/discharge cycles.

[0018]

[Problem to be Solved by the Invention]

For solving the problems of a reduced appearance capacity and deteriorated cycle properties seen in FIGs. 6 and 7, it is necessary to provide an optimal electrolyte composition ($H^+$, $X^-$), or to improve an electrode for preventing peroxidation-perreduction deterioration of an electrode active material in the reaction between an electrolyte and the active material. The above matters are issues for improving cycle properties.

[0019]

In both Prior arts 1 and 2, a nitrogen-containing heterocyclic compound is added to a non-aqueous electrolytic solution. In Prior art 3, a polymer gel electrolyte consisting of, for example, an aprotic solvent and a polyimidazole is used to make the electrolyte

unreactive to lithium in the negative electrode so that increase of an internal resistance can be minimized and thus cycle properties can be improved. In any of Prior arts 1, 2 and 3, a nitrogen-containing heterocyclic compound is added to an electrolyte, which is different from this invention where a particular substance is added and blended in an electrode.

[0020]

Since Prior art 4 relates to a lithium battery in which an electrolytic solution contains an organic solvent, a proton concentration is not taken into consideration. Thus, a mechanism of proton conductivity or deterioration as characteristics of an active material is considerably different. Prior art 4 is different from this invention in which an electrolytic solution contains a proton source and a proton-conducting polymer is used as an active material.

[0021]

An objective of this invention is to improve an electrode for preventing peroxidation-perreduction deterioration of an electrode active material and to provide a cell electrode exhibiting improved cycle properties and an electrochemical cell comprising the electrode.

[0022]

[Means for Solving the Problem]

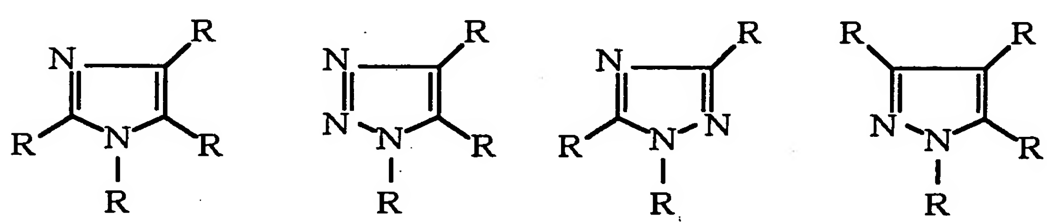
The cell electrode of this invention is characterized in that an active material in an electrode

material is a proton-conducting polymer and the electrode material comprises a nitrogen-containing heterocyclic compound.

[0023]

In the present invention, the nitrogen-containing heterocyclic compound comprises at least one material selected from nitrogen-containing hetrocyclic monomers and nitrogen-containing heterocyclic basic polymers; and the nitrogen-containing hetrocyclic monomer comprises at least one compound selected from the group of imidazole and their derivatives represented by formula (1), triazole and their derivatives represented by formulas (2) and (3), and pyrazole and their derivatives represented by formula (4).

[0024]



(1) (2) (3) (4)

[0025]

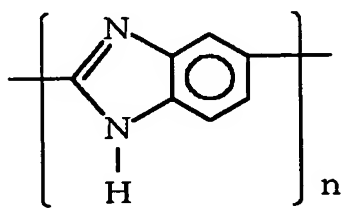
wherein Rs independently represent hydrogen, alkyl having 1 to 4 carbon atoms, amino, carbonyl, nitro, phenyl, vinyl, halogen, acyl, cyano, trifluoromethyl, alkylsulfonyl or trifluoromethylthio.

[0026]

The nitrogen-containing basic polymer comprises at

least one member selected from the group consisting of polybenzimidazole, polyvinylimidazole, polybenzbisimidazole and polyimidazole, besides polybenzimidazole represented by formula (5) or polyvinylimidazole represented by formula (6) as the polymer:

[0027]



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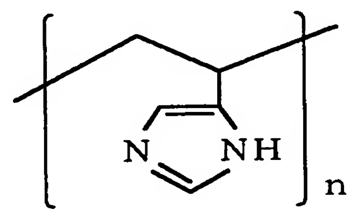


(6)

wherein n represents a positive integer.

[0028]

Further, the proton-conducting polymer as a constituent of the electrode may incorporate a proton-conducting nitrogen-containing basic polymer obtained by the copolymerization of the starting material of the proton-conducting polymer and a nitrogen-containing heterocyclic compound, which copolymer may be usable as an active material in an electrode, and the mixture of the copolymer and another proton-conducting polymer.

[0029]

The constitution of the secondary cell or capacitor in the present invention is characterized in that the above material is used as an electrode, on one side or both sides, and the proton-conducting polymer is contained as an active

material. An electrolyte containing a proton source may be used as the electrolytic solution in this invention.

[0030]

[Modes for carrying out the invention]

Preferred embodiments of this invention will be detailed. This invention is characterized in that a cell electrode is made of an electrode material comprising a proton-conducting polymer as an active material and a nitrogen-containing heterocyclic compound. The constitution of the cell according to this invention is the same as conventional ones.

[0031]

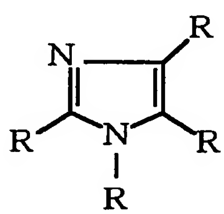
As shown in FIG. 1, a positive electrode 2 comprising a proton-conducting polymer as an active material and a negative electrode 3 are formed on a positive current collector 1 and a negative current collector 4, respectively, and these electrodes are laminated via a separator 5. Protons only serve as an electric-charge carrier. The cell is filled with an aqueous or non-aqueous solution containing a proton source as an electrolytic solution and is sealed by a gasket 6.

[0032]

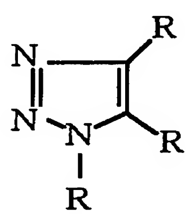
The electrodes 2, 3 can be formed as follows. A powdery doped or undoped proton-conducting polymer is blended with a conductive auxiliary and a binder to prepare a slurry, which is then placed in a mold with a desired size and molded by a hot press to form an electrode having

a desired electrode density and a desired film thickness. Then, a positive electrode and a negative electrode thus formed are mutually faced via a separator to give a cell. The electrode characteristically comprises the nitrogen-containing heterocyclic compound represented by chemical formulas (1) to (4).

[0033]



(1)



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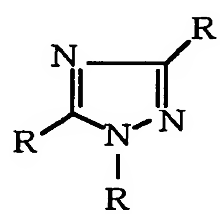

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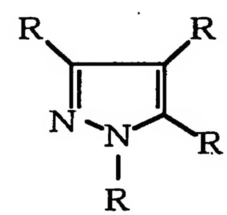


(4)

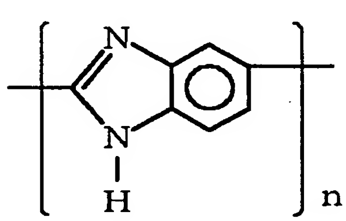
[0034]

wherein Rs independently represent hydrogen, alkyl having 1 to 4 carbon atoms, amino, carbonyl, nitro, phenyl, vinyl, halogen, acyl, cyano, trifluoromethyl, alkylsulfonyl and trifluoromethylthio.

[0035]

Also, the electrode characteristically comprises the nitrogen basic polymer represented by chemical formula (5) or (6):

[0036]



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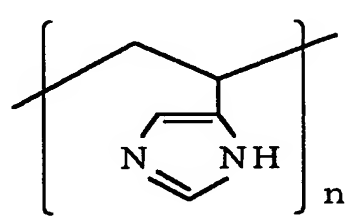


(6)

[0037]

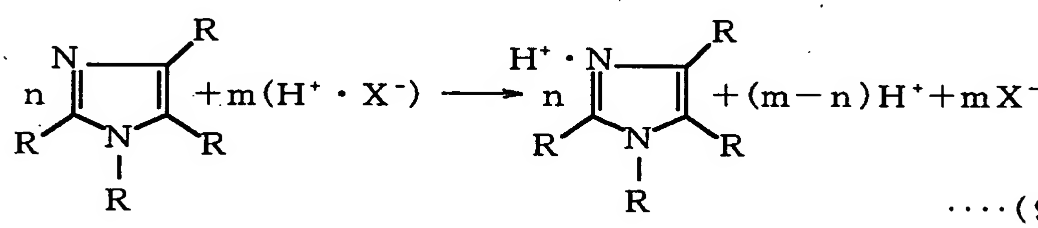
wherein n represents a positive integer.

nitrogen basic polymers such as polybenzimidazole, polyvinylimidazole, polybenbisimidazole and polyimidazle are also usable.

[0038]

Using such an electrode, a reaction described below may occur with ions in an electrolytic solution containing a proton source. When the nitrogen-containing heterocyclic compound is imidazole, imidazole adsorbs a proton as shown in chemical formula (9).

[0039]



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[0040]

wherein n represents an integer and m represents an integer larger than n.

[0041]

Such proton adsorption by imidazole results in prevention of peroxidation or perreduction of an active material of positive/negative electrode and thus a longer cycle life. As described above, a concentration of protons involved in a reaction with an active material may be appropriately adjusted by controlling the amount of a

nitrogen-containing heterocyclic compound or nitrogen basic polymer to be added and blended, without varying a concentration of an anion to be a dopant. Thus, a higher appearance capacity can be maintained and cycle properties can be improved.

[0042]

An electrode comprising the proton-conducting nitrogen basic polymer, which is obtained by copolymerization of the monomer of proton-conducting polymer and a nitrogen-containing heterocyclic compound, as an electrode active material can exhibit improvement equivalent to that achieved by the electrode described above (the active material with the additive, (1) to (4), (5) (6)). Further, the copolymer is an effective material for an electrode where peroxidation-perreduction deterioration is much more reduced in comparison with a conventional electrode as described later even under a high proton concentration atmosphere.

[0043]

For determining the effects of this invention, a positive electrode (comprising an indole trimer as an active material) was evaluated by cyclic voltammetry (CV-measurement). In this measurement, a working electrode was an electrode formed by depositing a mixture of an active material of positive electrode with imidazole on a carbon sheet; a counter electrode was a platinum electrode; and a reference electrode was an Ag/AgCl electrode. A measuring

temperature was 25 °C, a scan voltage ranged from 600 to 1100 mV, and a scan speed was 1 mV/sec. An electrolytic solution was a 20 wt% aqueous solution of sulfuric acid, and a composition of a positive electrode material as the working electrode was that described in Example 3, that is, containing 20 wt% of imidazole based on the weight of the positive active material. An electrode without imidazole (Comparative Example 1 described later) was also evaluated as a reference example. The results are shown in a graph of discharge capacity variations in FIG. 2.

[0044]

The results show that a redox potential in Example 3 was shifted to lower potential side by several tens of mV in relation to Comparative Example 1. That is, shift to a stable potential at which oxidation deterioration is reduced was observed. It may be concluded that a cycle life was prolonged.

[0045]

An active material of negative electrode (polyphenylquinoxaline) was also evaluated by CV measurement using the negative electrodes described in Example 3. FIG. 3 shows the results of variation in their discharge capacity. The results show that deterioration in a capacity, involving elution of the active material, due to excessive protonation of the active material of negative electrode was inhibited.

It was, therefore, shown that this invention can

prevent deterioration in both electrodes, a positive electrode and a negative electrode.

[0046]

Although an aqueous electrolyte solution is described in this invention, any electrolyte comprising a proton source can bring forth the same effect. The same effect (prevention of deterioration of active material) is also observed in the cell electrodes that comprises either the nitrogen-containing heterocyclic compounds (the above (1) (2) (3) (4)) or nitrogen-containing basic polymers (the above (5), (6)) to be added and mixed. No particular limitation is set on the nitrogen atom in the heterocycle of substances (the above (1) to (4)). Although at lest one of compounds, the above (1) to (6), is preferable, a mixture of plural kinds may be used.

[0047]

The active material, the proton-conducting nitrogen-containing basic polymer obtained by copolymerizing the monomer of proton-conducting polymer with the nitrogen-containing heterocyclic compound, in the electrode is effective in the improvement of cycle characteristics as well as the case of incorporation of one of compounds, (1) (2) (3) (4) (5) and (6).

[0048]

An electrode active material constituting a cell electrode of this invention may be a proton-conducting polymer illustrated in the description of prior art.

Examples of active material of positive electrode is preferably selected from the group consisting of polyaniline, polydianiline, polydiaminoanthraquinone, polybiphenylaniline, polynaphthylaniline, polyindole, indole trimer and their derivatives. An active material of negative electrode is preferably selected from the group consisting of polypyridine, polypyrimidine, polyquinoxaline and their derivatives. In particular, preferred is a combination of an indole trimer and polyphenylquinoxaline.

[0049]

An electrolyte in this invention may be any electrolyte containing a proton source, preferably an aqueous solution of sulfuric acid.

[0050]

A content of compounds, the above (1) to (6), to be added in a cell electrode may be appropriately selected and does not be limited. If it is too low, oxidation deterioration of an active material may be inadequately inhibited. If the content is too high, an appearance capacity may be reduced, leading to deterioration in other properties. The content is, depending on the kind and concentration of the electrolyte and the kind of the substances added and blended, preferably 1 to 80 wt% to 100 wt% of the active material.

[0051]

This invention will be described with reference to, but not limited to, examples, and variations may be

acceptable in this invention without departing from the gist of this invention. There will be described examples of application to a secondary battery, but this invention may be suitably applied to another electrochemical cell such as an electric double layer capacitor by properly adjusting parameters such as a capacity and a charge/discharge rate.

[0052]

(Example 1)

A positive electrode was prepared as follows. To indole trimer as an active material were added 13 wt% of vapor growth carbon (VGCF) as a conductive auxiliary and 8 wt% of a polyfluorovinylidene (average molecular weight: 1100) as an electrode molding component. To 100 wt% of the mixture was added 5 wt% of imidazole. The resultant mixture was stirred and blended in a blender and then molded by a hot press into a solid electrode having a desired size, which was used as a positive electrode 2.

[0053]

A negative electrode was prepared as follows. To polyphenylquinoxaline as an active material were added 25 wt% of carbon black (K.B.600) as a conductive auxiliary. To 100 wt% of the mixture was then added 5 wt% of imidazole. The resultant mixture was stirred and blended in a blender and then molded by a hot press into a solid electrode having a desired size, which was used as a negative electrode 3. An electrolytic solution was a 20 wt% aqueous

solution of sulfuric acid.

[0054]

A separator 5 used was a polyolefin-based porous membrane or a cation-exchange membrane with a thickness of 10 to 50 μm. The positive electrode and the negative electrode were laminated together via a separator such that their electrode surfaces mutually faced, and a gasket was mounted to form a battery as shown in FIG. 1.

[0055]

(Example 2)

A positive electrode was prepared without adding substances ((1) to (3)). A negative electrode was prepared adding 20 wt% of imidazole. A 20 wt% aqueous sulfuric acid solution was used as an electrolytic solution. A battery was formed as described in Example 1 except for the above matters.

[0056]

(Example 3)

A positive electrode was prepared adding 20 wt% of imidazole. A negative electrode was prepared adding 20 wt% of imidazole. A 20 wt% aqueous sulfuric acid solution was used as an electrolytic solution. A battery was formed as described in Example 1 except for the above matters.

[0057]

(Example 4)

A positive electrode was prepared adding 50 wt% of imidazole. A negative electrode was prepared adding 50 wt%

of imidazole. A 20 wt% aqueous sulfuric acid solution was used as an electrolytic solution. A battery was formed as described in Example 1, except for the above matters.

[0058]

(Example 5)

A positive electrode was prepared adding 20 wt% of imidazole. A negative electrode was prepared adding 20 wt% of 1,2,4-triazole. A 20 wt% aqueous sulfuric acid solution was used as an electrolytic solution. A battery was formed as described in Example 1, except for the above matters.

[0059]

(Example 6)

A positive electrode was prepared adding 20 wt% of 2-phenylimidazole. A negative electrode was prepared adding 20 wt% of 2-phenylimidazole. A 20 wt% aqueous sulfuric acid solution was used as an electrolytic solution. A battery was formed as described in Example 1, except for the above matters.

[0060]

(Example 7)

A positive electrode was prepared adding 20 wt% of 3-trifluoromethylbenzimidazole. A negative electrode was prepared adding 20 wt% of 3-trifluoromethylbenzimidazole. A 20 wt% aqueous sulfuric acid solution was used as an electrolytic solution. A battery was formed as described in Example 1, except for the above matters.

[0061]

(Example 8)

A positive electrode was prepared adding 20 wt% of imidazole. A negative electrode was prepared adding 20 wt% of 3-trifluoromethylbenzimidazole. A 20 wt% aqueous sulfuric acid solution was used as an electrolytic solution. A battery was formed as described in Example 1, except for the above matters.

[0062]

(Example 9)

A positive electrode was prepared adding 10 wt% of imidazole and 10 wt% of 1,2,4-triazole. A negative electrode was prepared adding 20 wt% of 1,2,4-triazole instead of the imidazole. A 20 wt% aqueous sulfuric acid solution was used as an electrolytic solution. A battery was formed as described in Example 1, except for the above matters.

[0063]

(Example 10)

A positive electrode was prepared adding 10 wt% of imidazole and 10 wt% of 3-trifluoromethylbenzimidazole. A negative electrode was prepared adding 10 wt% of 1,2,4-triazole and 10 wt% of 3-trifluoromethylpyrazole. A 20 wt% aqueous sulfuric acid solution was used as an electrolytic solution. A battery was formed as described in Example 1, except for the above matters.

[0064]

(Example 11)

A positive electrode was prepared adding 60 wt% of imidazole. A negative electrode was prepared adding 60 wt% of imidazole. A 30 wt% aqueous sulfuric acid solution was used as an electrolytic solution. A battery was formed as described in Example 1, except for the above matters.

[0065]

(Example 12)

A positive electrode was prepared without adding any of the substances ((1) to (3)). A negative electrode was prepared adding 5 wt% of polybenzimidazole. A 20 wt% aqueous sulfuric acid solution was used as an electrolytic solution. A battery was formed as described in Example 1, except for the above matters d.

[0066]

(Example 13)

A positive electrode was prepared adding 5 wt% of polybenzimidazole. A negative electrode was prepared adding 5 wt% of polybenzimidazole. A 20 wt% aqueous sulfuric acid solution was used as an electrolytic solution. A battery was formed as described in Example 1, except for the above matters.

[0067]

(Example 14)

A positive electrode was prepared adding 20 wt% of polybenzimidazole. A negative electrode was prepared adding 20 wt% of polybenzimidazole. A 20 wt% aqueous sulfuric acid solution was used as an electrolytic solution.

A battery was formed as described in Example 1, except for the above matters.

[0068]

(Example 15)

A positive electrode was prepared adding 20 wt% of polyvinylimidazole. A negative electrode was prepared adding 20 wt% of polyvinylimidazole. A 20 wt% aqueous sulfuric acid solution was used as an electrolytic solution. A battery was formed as described in Example 1, except for the above matters.

[0069]

(Example 16)

A positive electrode was prepared adding 10 wt% of polybenzimidazole and 10 wt% of polyvinylimidazole. A negative electrode was prepared adding 20 wt% of polyvinylimidazole. A 20 wt% aqueous sulfuric acid solution was used as an electrolytic solution. A battery was formed as described in Example 1, except for the above matters.

[0070]

(Example 17)

A positive electrode was prepared adding 20 wt% of imidazole. A negative electrode was prepared adding 10 wt% of polybenzimidazole and 10 wt% of polyvinylimidazole. A 20 wt% aqueous sulfuric acid solution was used as an electrolytic solution. A battery was formed as described in Example 1, except for the above matters.

[0071]

(Example 18)

A positive electrode was prepared as adding 20 wt% of 3-trifluoromethylpyrazole. A negative electrode was prepared adding 10 wt% of polybenzimidazole and 10 wt% of polyvinylimidazole. A 20 wt% aqueous sulfuric acid solution was used as an electrolytic solution. A battery was formed as described in Example 1, except for the above matters.

[0072]

(Example 19)

A positive electrode was prepared without adding any of the substances ((1) to (3)). 3,3-diaminobenzidine (DABZ) and 1,4-bisbenzil (BBZ) for condensation polymerization were used as materials for an active material of a negative electrode. The negative electrode was prepared adding a proton-conducting polymer having an imidazole ring which was prepared by copolymerization of materials for the active material, which comprise 1,4-bisbenzil (BBZ) and a nitrogen-containing heterocyclic compound. A 20 wt% aqueous sulfuric acid solution was used as an electrolytic solution. A battery was formed as described in Example 1, except for the above matters.

[0073]

(Example 20)

A positive electrode was prepared adding 1,2,4-triazole. A negative electrode was prepared as described

in Example 19. A 20 wt% aqueous sulfuric acid solution was used as an electrolytic solution. A battery was formed as described in Example 1, except for the above matters.

[0074]

(Example 21)

A positive electrode was prepared adding 1,2,4-triazole. A negative electrode was prepared adding 10 wt% of a proton-conducting polymer as obtained in Example 19. A 20 wt% aqueous sulfuric acid solution was used as an electrolytic solution. A battery was formed as described in Example 1, except for the above matters.

[0075]

(Comparative Example 1)

Electrodes were prepared as described in Example 1 without adding any of the substances ((1) to (3)), in either electrode. A battery was formed as described in Example 1, except these electrodes were used.

[0076]

(Comparative Example 2)

Electrodes were prepared as described in Example 1 without adding any of the substances ((1) to (3)), in either electrode. A 30 wt% aqueous sulfuric acid solution was used as an electrolytic solution. A battery was formed as described in Example 1, except these electrodes and the electrolytic solution were used.

[0077]

The batteries prepared in Examples 1 to 20 and

Comparative Examples 1 and 2 were evaluated for an appearance capacity and cycle properties. The results are shown in Table 1.

[0078]

Table 1

| | Appearance capacity (%) | Cycle properties (%) | Cell internal resistance variation ratio(%) |
|---|---|---|---|
| Exam. 1 | 98.4 | 83.4 | 118 |
| Exam. 2 | 99.9 | 82.6 | 119 |
| Exam. 3 | 97.2 | 88.3 | 111 |
| Exam. 4 | 85.8 | 90.5 | 107 |
| Exam. 5 | 100.1 | 84.6 | 115 |
| Exam. 6 | 99.9 | 85.7 | 115 |
| Exam. 7 | 100.1 | 86.8 | 115 |
| Exam. 8 | 97.8 | 82.1 | 119 |
| Exam. 9 | 102.3 | 86.7 | 115 |
| Exam. 10 | 99.4 | 85.2 | 115 |
| Exam. 11 | 99.9 | 82.9 | 119 |
| Exam. 12 | 100.9 | 85.6 | 114 |
| Exam. 13 | 102.1 | 88.8 | 111 |
| Exam. 14 | 101.5 | 93.4 | 106 |
| Exam. 15 | 100.6 | 93.2 | 106 |
| Exam. 16 | 100.1 | 90.8 | 109 |
| Exam. 17 | 100.1 | 86.7 | 112 |
| Exam. 18 | 99.8 | 86.4 | 113 |
| Exam. 19 | 104.2 | 94.9 | 105 |
| Exam. 20 | 102.8 | 96.4 | 104 |
| Exam. 21 | 101.3 | 95.2 | 102 |
| Comp. Exam. 1 | 100.0 | 80.1 | 121 |
| Comp. Exam. 2 | 102.6 | 65.0 | 138 |

[0079]

In Table 1, an appearance capacity is calculated to an appearance capacity in Comparative Example 1 as 100 %. Cycle properties is expressed as a discharge capacity variation (measured at 25 °C) after 10,000 cycles. Cell

internal resistance variation ratio is a variation of a direct-current resistance of a cell according to cycle number, which is a value (%) that is obtained by the following: (a direct-current resistance at the initiation of the cycles / a direct-current resistance after 10,000 cycles) × 100. Cycle conditions were as follows; charging: CCCV charge at 1A and 1.2 V for 10 min, discharging: CC discharge at 0.2 A (equivalent to 1C), and final voltage: 0.8 V.

[0080]

FIGs. 4 and 5 show the evaluation results of Examples 1, 3, 5, 7, 14 and 19 and Comparative Examples 1 and 2 for cycle properties and cell internal resistance variation ratio. As seen from discharge capacity variation in FIG. 4, as the cycle number increased, a discharge capacity variation was reduced to 80 % and 65 % in Comparative Examples 1 and 2, respectively, while discharge capacity variations in Examples 1-19 were less reduced to 85 % to 96 %. It indicates that a discharge capacity is less varied in Examples.

[0081]

As seen from cell internal resistance variation ratio in FIG. 5, cell internal resistance variation ratios in Examples 1, 3, 5, 7, 14 and 19 were 105 to 116 %, while cell internal resistance variation ratios in Comparative Examples 1 and 2 were 121 % and 138 %, respectively. It indicates that cell internal resistance variation in

Examples is less than that in Comparative Example 1 or 2. These results show that this invention can improve cycle properties while inhibiting reduction in an appearance capacity.

[0082]

Although these Examples employ indole trimer or polyphenylquinoxaline as an active material, an active material is not limited to those, but any polymer having proton conductivity may be used, an active material is not limited to those.

[0083]

[Effect of the Invention]

This invention can improve cycle properties while inhibiting reduction in an appearance capacity. This is because a nitrogen-containing heterocyclic compound or basic polymer added to an electrode interacts with protons in an electrolytic solution so that only a proton concentration can be controlled without reducing a concentration of anions acting as dopant in an adsorption-desorption reaction between the active material and protons in the electrolyte. It is also because an optimal proton-concentration atmosphere for the reaction can be created, resulting in inhibition of deterioration due to peroxidation.

[Brief Description of the Drawings]

FIG. 1 is a cross section of an electrochemical cell according to an embodiment of this invention.

FIG. 2 is a graph showing CV measurement results for a positive electrode in an aqueous sulfuric acid solution using electrodes according to this invention and according to the prior art.

FIG. 3 is a graph showing CV measurement results for a negative electrode in an aqueous sulfuric acid solution using electrodes according to this invention and according to the prior art.

FIG. 4 is a graph showing variation in cycle properties for cells using electrodes according to this invention (Examples 1, 3, 5, 7, 14 and 19 and according to the prior art (Comparative Examples 1 and 2).

FIG. 5 is a graph showing variation in a cell internal resistance vs cycle number for cells using electrodes according to this invention (Examples 1, 3, 5, 7, 14 and 19) and according to the prior art (Comparative Examples 1 and 2).

FIG. 6 is a graph showing variation in cycle properties for different sulfuric acid concentrations.

FIG. 7 is a graph showing variation in an appearance capacity for different sulfuric acid concentrations.

[Reference Numerals]

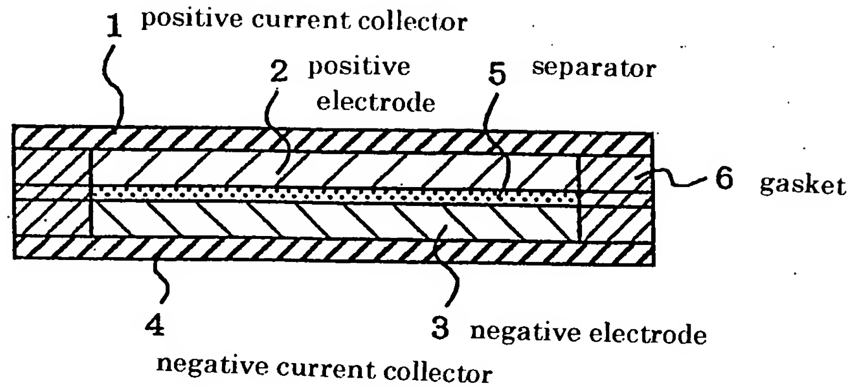
| | |
|---|---|
| 1 | positive current collector |
| 2 | positive electrode |
| 3 | negative electrode |
| 4 | negative current collector |

5 separator

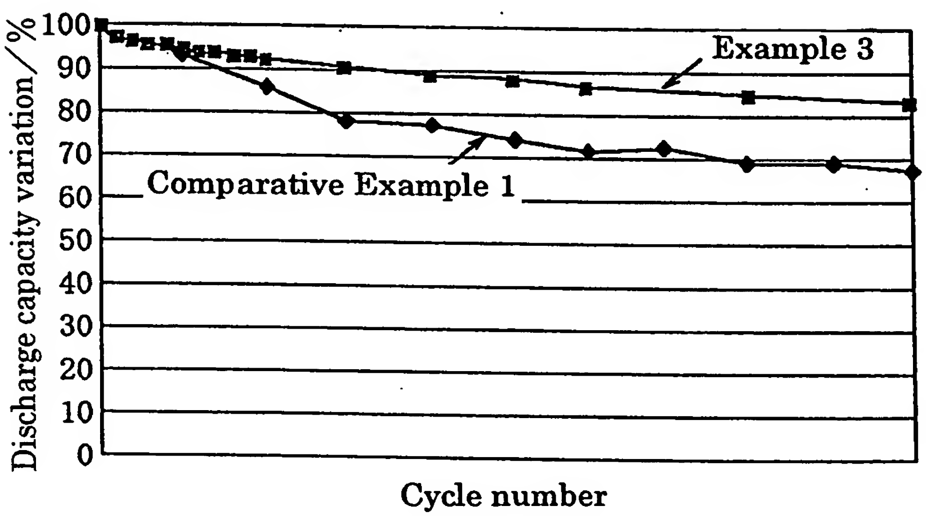
6 gasket

[Document Name] Drawings

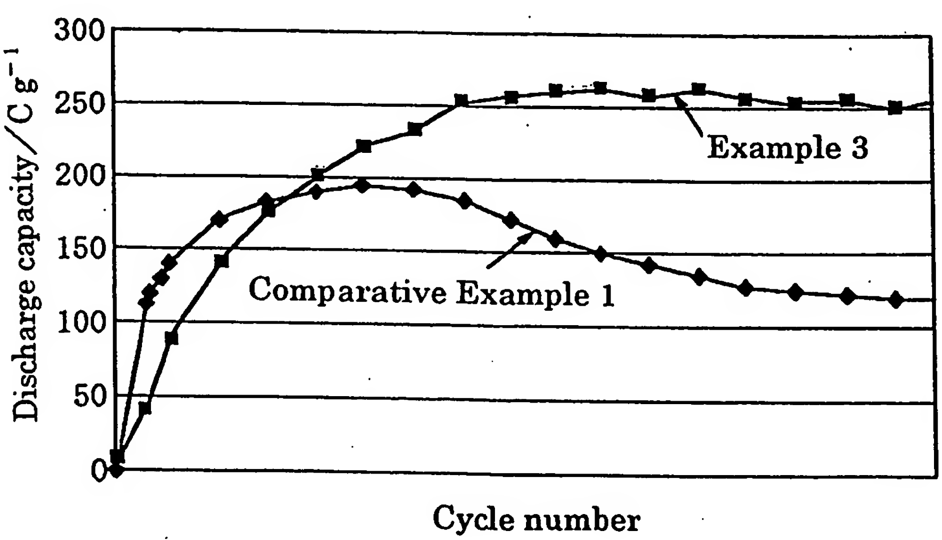
[FIG. 1]



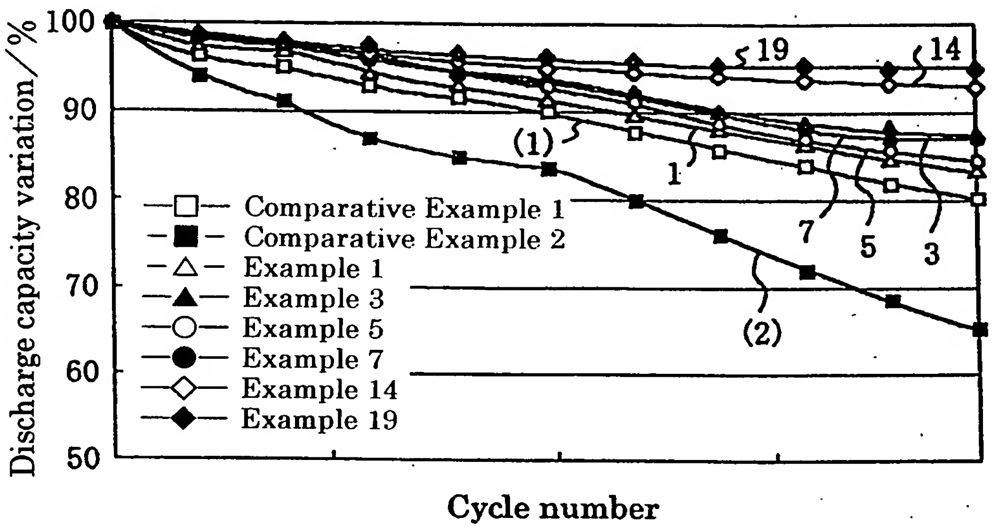

[FIG. 2]



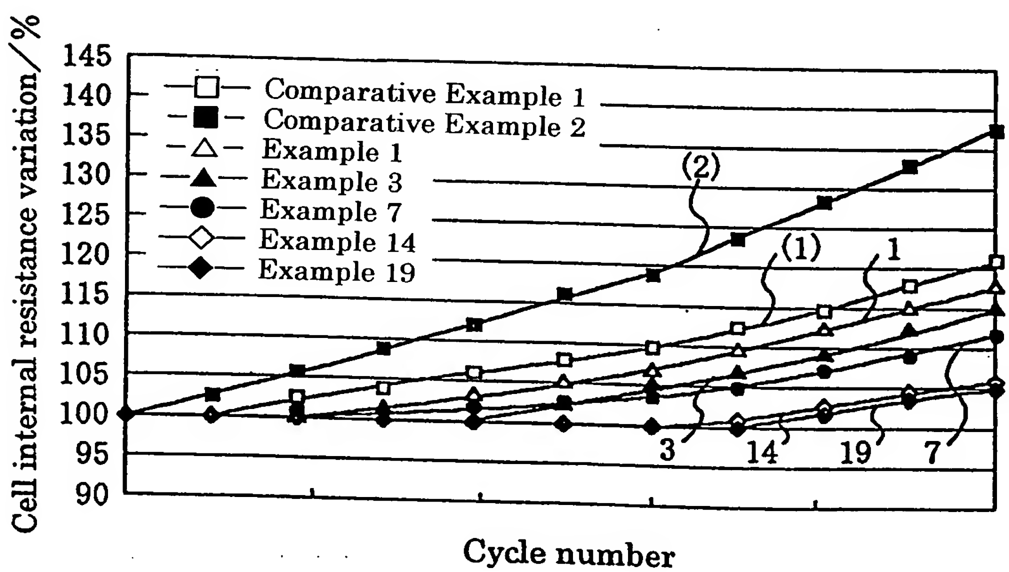

[FIG. 3]



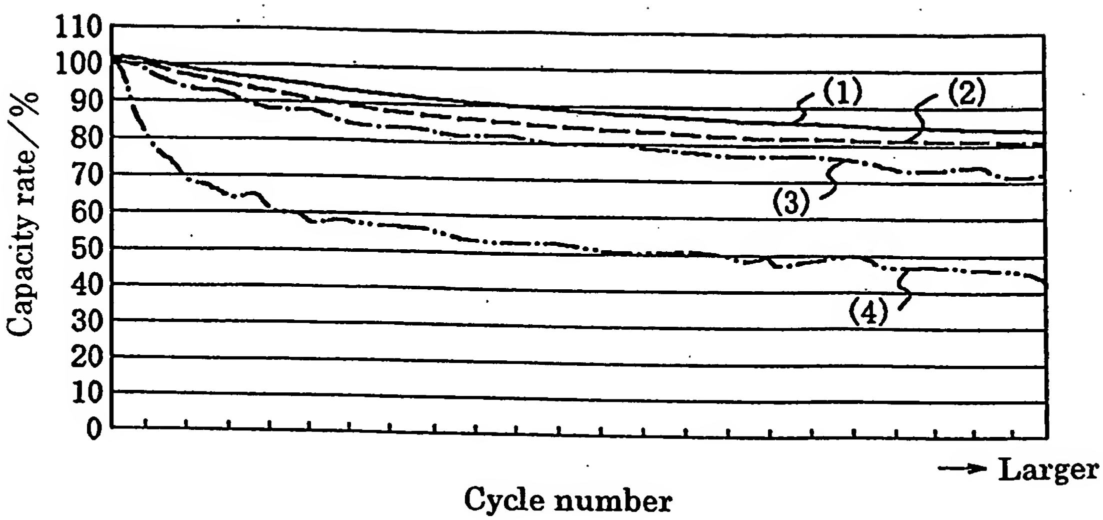
[FIG. 4]


Discharge capacity variation／%
100
90
80
70
60
50
Cycle number
Comparative Example 1
Comparative Example 2
Example 1
Example 3
Example 5
Example 7
Example 14
Example 19
19
14
(1)
1
7
5
3
(2)

[FIG. 5]

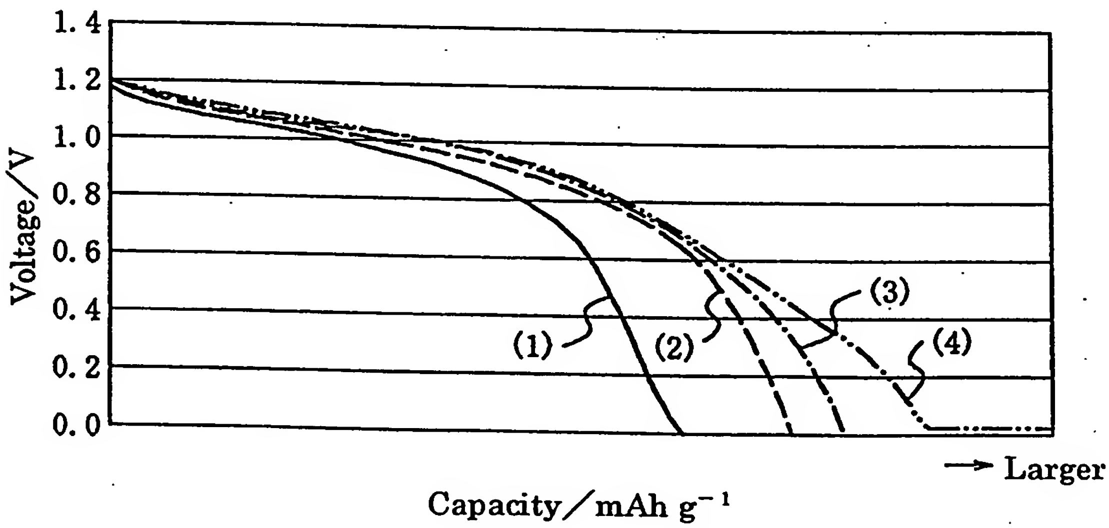

Cell internal resistance variation／%
145
140
135
130
125
120
115
110
105
100
95
90
Cycle number
Comparative Example 1
Comparative Example 2
Example 1
Example 3
Example 7
Example 14
Example 19
(2)
(1)
1
3
14
19
7

[FIG. 6]




(1) : 0. 5mol/L (2) : 1. 5mol/L
(3) : 2. 0mol/L (4) : 3. 6mol/L

[FIG. 7]




(1) : 0. 5mol/L (2) : 1. 5mol/L
(3) : 2. 0mol/L (4) : 3. 6mol/L

[Document Name] Abstract

[Abstract]

[Problem] An objective of this invention is to improve an electrode for preventing peroxidation-perreduction deterioration of an electrode active material and to provide a cell electrode exhibiting improved cycle properties.

[Solution] The material of electrodes (2, 3) characteristically comprises an active material consisting of a proton-conducting polymer comprising a nitrogen-containing heterocyclic compound. The nitrogen-containing heterocyclic compound comprises at least one of nitrogen-containing heterocyclic monomers and nitrogen-containing heterocyclic basic polymers, also the proton-conducting polymer constituting electrodes can be a proton-conducting nitrogen-containing basic polymer obtained by copolymerization of the material for the proton-conducting polymer and the nitrogen-containing heterocyclic compound.

[Selected Drawing] FIG. 1